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Synthesis, crystal structures and photophysical properties investigations of two new

pyridinium complexes containing [Sm(TTA)₄]⁻ and [Eu(TTA)₄]⁻

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Abstract

Two new lanthanide(III) complexes were designed and synthesized: DAS[M(TTA)₄]⁻, (M = Sm, (1), M = Eu, (2)), each of them contained one trans-4-[4'-(N, N-dimethylamino)styryl]-N-methyl pyridinium (DAS) cationic moity, four 2-thenoyltrifluoroacetone anions (TTA-), and one cationic lanthanide(III). Herein, the structures were confirmed by single crystal X-ray diffraction analysis. The results revealed that the central lanthanide (III) atom was fashionable eight-coordinated with square-antiprismatic coordination environment. Meanwhile, the photophysical properties of 1 and 2 were investigated by fluorescence (FL) spectra. It was proposed that there was antenna effect and the energy transfer took place from the DAS cationic moity to lanthanide (III) ions.

Keywords

Samarium(III) complex; Europium(III) complex; Fluorescence spectra; X-ray diffraction analysis; Energy transfer

² ACCEPTED MANUSCRIPT

1. Introduction

The luminescence of lanthanide(III) complexes had raised considerable interest, owing to their unique luminescence properties, high color purity, long luminescence lifetimes, and insensitivity to environmental quenching.^[1-6] And they also had potential applications in biological systems, optical amplification, magnetic properties luminescent materials.^[7-12]

In fact, the emission color depended on the lanthanide ion, but was mostly up to the environment of a given lanthanide ion.^[13] To the best of our knowledge, that lanthanides(III) had affinity to donor atoms, so the ligands including oxygen atoms could be widely used in the synthesis of lanthanide complexes. ^[14] In addition, as for 2-thenoyltrifluoroacetone (HTTA), which had the structure of β -diketonatecan, could play a great role in constructing molecular frameworks as building block and it had much better advantages of transporting energy to lanthanide(III). ^[13]

Notably, organic pyridinium salts molecules tended to interact with another neighboring molecules through intramolecular charge balance, which could obtain a large conjugated structures.^[15] They pertained to the frequent use of designing various chemosensors for some highly specific metal ions, fluorescent probes for DNA and RNA detection in biological systems, single-molecule magnets as well as photodynamic cancer therapy.^[16-23]

The structures with the type of Q^+ [Ln(TTA)₄]⁻ were studied a lot,^[24] however, it was a great challenge to search for new luminescent materials. Spurred by the idea, we had synthesized

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DAS[M(TTA)₄], (M = Sm, (1), M = Eu, (2)), which were supposed to open up new characteristics and intriguing applications with a light-harvesting antenna.

2. Experimental section

2.1 Measurements and Methods

Chemical reagents used in the study were bought of analytical grade, and some of them were synthesized and purified. Mass spectra were obtained with MALDI-TOF-MS. IR spectra were located from NEXUS 870 (Nicolet) spectrophotometer in the range of 400-4000 cm⁻¹ using a powder sample on a KBr plate. Fluorescence spectra of solid state were determined by F-4500 FL Spectrophotometer.

2.2 Crystal Structure Determination and Refinement

X-ray diffraction data were collected on a Bruker Smart 1000 CCD area detector diffractometer. Both of the radiation sources were MoK_{α} ($\lambda = 0.71073$ Å). Empirical absorption correction was applied to the data. The structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 . All the nonhydrogen atoms were located from the trial structure and then refined anisotropically by SHELXTL. All structures were solved by direct methods with SHELXL-97. The hydrogen atom positions were geometrically idealized and generated in idealized positions and fixed displacement parameters. Details of the crystal

parameters, data collections and refinements were listed in **Table 1**, and selected bond distances and angles of complexes **1** and **2** were given in **Table 2** and **Table 3**, respectively.

2.3 Synthesis of Complexes 1 and 2 (Scheme 1).

2.3.1 Preparation of 1,4-Dimethylpyridinium iodide

1,4-Dimethylpyridinium iodide was prepared according to a literature method^[25].

2.3.2 Preparation of Trans-4-[4'-(N, N-Dimethylamino)styryl]-N-methyl pyridinium iodide (DASI)

DASI was prepared according to the literature method ^[26].

2.3.3 Preparation of Samarium(III) complex (complex 1)

Complex **1** was prepared according to a literature method ^[27]. Obtained orange powder with yield of 43%. Found: M⁺ (MS/ESI), 1034.121. Anal. Calc. for C₄₈H₃₅F₁₂N₂O₈S₄Sm (%): C, 45.24; H, 2.77; N, 2.20. Found: C, 45.39; H, 2.68; N, 2.12. IR (KBr, cm⁻¹) selected bands: 3423 (s), 3083 (s), 2916 (s), 1603 (w), 1534 (m), 1476 (s), 1411(m), 1356 (s), 1302 (m), 1137 (m), 933 (s), 829 (s) 786 (s).

2.3.4 Preparation of Europium(III) complex (complex 2)

Complex 2 was prepared according to a literature method ^[27]. Afforded red powder with the yield of 40%. Found: M^+ (MS/ESI), 1035.076. Anal. Calc. for $C_{48}H_{35}EuF_{12}N_2O_8S_4$ (%): C, 45.18; H, 2.76; N, 2.20. Found: C, 45.29; H, 2.88; N, 2.17. IR (KBr, cm⁻¹) selected bands: 3444 (s),

3083 (s), 2916 (s), 1604 (w), 1577 (m), 1535 (m), 1509 (m), 1477(m), 1412 (s), 1357 (s), 1303 (m), 1136 (m), 936 (s), 828 (s), 785 (s).

Single crystals of complexes **1** and **2** were obtained by evaporating slowly of methanol solutions covered by acetonitrile at room temperature.

3. Results and Discussion

3.1 Crystal Structures of 1 and 2

As **Table 1** shown, complexes **1** and **2** were isomorphous and isostructural in the P2₁/n space group. Samarium was next to europium in the periodic table of elements, so they behaved similar in some certain aspects. From the data above, the Sm-O distances ranged from 2.339 (7) Å to 2.425 (6) Å, and the Eu-O distances ranged from 2.363 (5) Å to 2.426 (4) Å. Both of them had a distorted square antiprism environment around the lanthanide(III) site, with eight metal- oxygen bonds. In addition, in **Table 2**, the average bond lengths of C-O and the average of O-Eu-O angles of **1** (1.259 Å, 70.49°) were a little larger than that of in **Table 3** (1.255 Å, 70.38°), respectively, and the average of C-C-C angles of **1** (122.88°) was just a little smaller than that of **2** (123.08°).

According to X-ray crystallography, the crystal structures of complexes 1 and 2 were shown in **Fig.1** and **Fig.2**, and these structures were absolute equal except the lanthanide(III) cation moiety. The molecule unit was asymmetric with one lanthanide(III) ion coordinated closely with four bidentate TTA⁻ anions ligands and one pyridinium cation, and all hydrogen atoms were deleted from their previous positions. The anionic TTA⁻ appeared as typical O,O-chelates, which generated a new distorted square antiprism with the two square planes from (O1~O2~O5~O6) and (O3~O4~O7~O8). The Samarium(III) coordination environment with two distorted square antiprisms was shown in **Fig.3a** and that of Europium(III) complex was in **Fig.4a**. This kind of coordination configuration around lanthanide(III) was typical eight-coordinated, which leaded the low structural symmetry in complexes 1 and 2.

In the crystal, the neighboring molecules of **1** were linked by intermolecular S(1)-S(4)C(20)-H(20)...O(5) and C(10)-H(10)...F(4) hydrogen bonding interactions to form a one-dimensional structure as shown in **Fig.3b**. The distances of S(1)-S(4) C(20)-H(20)...O(5)and C(10)-H(10)...F(4) hydrogen bonds lengths were 3.5617 (5) Å, 2.7086 (6) Å and 2.6322 (13) Å, respectively. It also existed weak C–H... π , C(7)-H(7)...F(4) and C(30)-H(30)...H(16A)interactions. On the basis of **Fig.3b**, the adjacent layers were linked by C(6)-H(6)...C(18) (2.7908 (11) Å) bonding interactions to form two-dimensional packing diagram (**Fig.3c**). Furthermore, we could obtain three-dimensional crystal packing via weak C(18)-H(18)...C(27) (2.8773 (16) Å) intermolecular bonding under the help of the two-dimensional diagram (**Fig.3d**).

As for the one-dimensional chain of complex **2** was shown in **Fig.4b** via C(26)-H(26)···F(10) and C(42)-H(42)···F(12) are 2.5458 (9) Å and 2.6234 (10) Å, respectively. Similar with **1**, there were also C(38)-H(38)···F(12), C–H··· π , and C(45)-H(45)···C(13) interactions. The adjacent molecules were linked to each other via intermolecular C(39)-H(39)···C(3) and C(38)-H(38)···F(12) and C(26)-H(26)···F(10) (2.7757 (9) Å, 2.4651 (10) Å and 2.5488 (9) Å, respectively), which formed two-dimensional structure of **2** (**Fig.4c**). Three-dimensional packing diagram was generated via C(19)-H(19)···F(5) hydrogen bond on the basis of its two-dimensional layers, as shown in **Fig.4d**. The distance of hydrogen bond C(19)-H(19)···F(5) was 2.567 Å. All results revealed that hydrogen bonds were very important for molecules to form relevant multidimensional structures.

3.2 Fluorescence Spectra Studies

The spectroscopic studies were investigated by the fluorescence spectra in solid state. The emission spectra of pyridinium iodide (DASI, $\lambda_{ex} = 470$ nm), Sm(TTA)₄TBA ($\lambda_{ex} = 346$ nm), **1** ($\lambda_{ex} = 416$ nm) and **1** ($\lambda_{ex} = 470$ nm) were shown in **Fig. 5**. The emission spectra of pyridinium iodide (DASI, $\lambda_{ex} = 470$ nm), Eu(TTA)₄TBA ($\lambda_{ex} = 376$ nm), **2** ($\lambda_{ex} = 376$ nm), **2** ($\lambda_{ex} = 443$ nm) and **2** ($\lambda_{ex} = 470$ nm) were shown in **Fig. 6**. For the DASI, the characteristic band was at 670 nm. Characteristic bands from the Sm(III) cation were observed around 568 nm (${}^{5}G_{5/2} \rightarrow {}^{6}H_{5/2}$), 607 nm (${}^{5}G_{5/2} \rightarrow {}^{6}H_{7/2}$), 650 nm (${}^{5}G_{5/2} \rightarrow {}^{6}H_{9/2}$), respectively. And characteristic emission bands from the Eu(III) cation were about 594 nm (${}^{5}D_{0} \rightarrow {}^{7}F_{1}$), and 613 nm (${}^{5}D_{0} \rightarrow {}^{7}F_{2}$),

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respectively. The most strongest emission band of Sm(III) cation was at 607 nm (${}^{5}G_{5/2} \rightarrow {}^{6}H_{7/2}$) with orange light. However, Eu(III) cation was at 613 nm (${}^{5}D_{0} \rightarrow {}^{7}F_{2}$), emiting red light. Although the bands of complexes **1** and **2** were also around 590 nm and 670 nm, which were respectively from M(III) cations (M = Sm, M = Eu) and DASI, with much more intense emission bands. The results proposed that the energy transfer took place from DASI to lanthanide (III) ions with an antenna effect .

4. Conclusions

In summary, two new lanthanide(III) complexes were presented including the synthesis, structures and the fluorescence properties. From the single crystal X-ray diffraction analysis, lanthanide(III) site can be approximately described as a distorted square antiprism, with two square planes. The multidimensional structures of 1 and 2 were presented respectively. In addition, the results of fluorescence spectra revealed that characteristic emission bands of complexes 1 and 2 were from lanthanide(III) cations and pyridinium moity, which may supported that there was antenna effect and the energy transfer may took place from the DASI to the lanthanide(III) ions.

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¹² ACCEPTED MANUSCRIPT

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¹³ ACCEPTED MANUSCRIPT

	1	2
CCDC	981462	789624
Empirical formula	$C_{48}H_{35}SmF_{12}N_2O_8S_4$	$C_{48}H_{35}EuF_{12}N_2O_8S_4$
Formula weight	1274.37	1275.98
Crystal system	Monoclinic	Monoclinic
pace group Crystal size	P2 ₁ /n 0.30 x 0.20 x 0.2	₁ /n 0.17 x 0.12 x 0.11 m
	mm	
Unit cell dimensions	a= 10.497(5)Å	a= 10.491(5)Å
	b= 21.838 (5)Å	b= 21.840(5)Å
	c= 23.321 (5)Å	c= 23.324(5)Å
	β= 101.209 (5)°	β= 101.134(5)°
Volume	5244(3)Å ³	5243(3) Å ³
Z	4	4
$D_c \ (\mathrm{mg \ m}^{-3})$	1.614	1.616
μ (mm ⁻¹)	1.374	1.451
Reflns. Collected	25971	37429
Reflns. Unique	8999	12152
Parameters	679	698
Goodness-of-fit on F ²	1.088	0.990
R_1 , w R_2 [I>2sigma(I)]	$R_1 = 0.0694 \text{ w}R_2 =$	$R_1 = 0.0638 \text{ w} R_2 = 0.132$
	0.1553	

Table 1	Crystal da	ata and stru	cture refinement	s for compo	ounds 1 and 2.
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Sm(1)-O(1)	2.400(6)	Sm(1)-O(2)	2.425(6)
Sm(1)-O(3)	2.379(6)	Sm(1)-O(4)	2.396(6)
Sm(1)-O(5)	2.396(6)	Sm(1)-O(6)	2.413(6)
Sm(1)-O(7)	2.339(7)	Sm(1)-O(8)	2.407(6)
O(1)-C(43)	1.244(11)	O(2)-C(45)	1.239(12)
O(3)-C(46)	1.283(11)	O(4)-C(48)	1.261(11)
O(5)-C(39)	1.251(11)	O(6)-C(37)	1.216(11)
O(7)-C(40)	1.295(12)	O(8)-C(42)	1.250(11)
O(1)-Sm(1)-O(2)	70.4(2)	O(3)-Sm(1)-O(4)	70.9(2)
O(5)-Sm(1)-O(6)	70.3(2)	O(7)-Sm(1)-O(8)	69.9(2)
C(39)-C(38)-C(37)	122.2(9)	C(42)-C(41)-C(40)	123.4(9)
C(45)-C(44)-C(43)	123.0(10)	C(46)-C(47)-C(48)	123.7(9)

Table 2. Selected bond lengths (Å) and angles (°) for compound 1

¹⁵ ACCEPTED MANUSCRIPT

Eu(1)-O(1)	2.426(4)	Eu(1)-O(2)	2.375(4)
Eu(1)-O(3)	2.380(4)	Eu(1)-O(4)	2.383(4)
Eu(1)-O(5)	2.402(4)	Eu(1)-O(6)	2.384(5)
Eu(1)-O(7)	1.282(7)	Eu(1)-O(8)	2.363(5)
O(1)-C(7)	1.247(8)	O(2)-C(5)	1.255(7)
O(3)-C(13)	1.242(7)	O(4)-C(15)	1.254(8)
O(5)-C(21)	1.242(7)	O(6)-C(23)	1.273(8)
O(7)-C(31)	1.262(7)	O(8)-C(29)	1.257(8)
O(2)-Eu(1)-O(1)	69.95(14)	O(3)-Eu(1)-O(4)	70.61(15)
O(6)-Eu(1)-O(5)	70.48(16)	O(8)-Eu(1)-O(7)	70.92(16)
C(7)-C(6)-C(5)	121.9(6)	C(15)-C(14)-C(13)	123.5(7)
C(23)-C(22)-C(21)	122.3(7)	C(31)-C(30)-C(29)	123.8(6)

Table 3. Selected bond lengths (Å) and angles (°) for compound 2



Fig.1. The molecular structure of complex 1; H atoms are omitted for clarity.

¹⁷ ACCEPTED MANUSCRIPT



Fig.2. The molecular structure of complex 2; H atoms are omitted for clarity.

¹⁸ ACCEPTED MANUSCRIPT



Fig.3. (a) The distorted square antiprism of Sm(III) coordination environment; (b) 1D structure of complex 1 showing the weak interactions; (c) 2D structure of complex 1 showing the weak interactions; (d) 3D structure of complex 1 showing the weak interactions; (In order to clear,

hydrogen atoms are deleted)

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Fig.4. (a) The distorted square antiprism of Eu(III) coordination environment; (b) 1D structure of complex 2 showing the weak interactions; (c) 2D structure of complex 2 showing the weak interactions; (d) 3D structure of complex 2 showing the weak interactions; (In order to clear,

hydrogen atoms are deleted)

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Fig.5. The emission spectra of pyridinium iodide (DASI, $\lambda_{ex} = 470 \text{ nm}$), Sm(TTA⁻)₄TBA ($\lambda_{ex} = 346 \text{ nm}$), 1 ($\lambda_{ex} = 346 \text{ nm}$), 1 ($\lambda_{ex} = 470 \text{ nm}$) and 1 ($\lambda_{ex} = 416 \text{ nm}$) in the solid state.

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Fig.6. The emission spectra of pyridinium iodide (DASI, $\lambda_{ex} = 470$ nm),

Eu(TTA⁻)₄TBA (λ_{ex} = 376 nm), 2 (λ_{ex} = 376 nm), 2 (λ_{ex} = 470 nm) and 2 (λ_{ex} = 443 nm) in

solid state.





DAS $[M (TTA)_4], M = Sm, (1); M = Eu, (2)$

Scheme 1 Synthesis routes of complexes 1 and 2.

²³ ACCEPTED MANUSCRIPT